

CHAPTER III

EXPERIMENTALS

3.1 Chemicals

Chemicals	Company
Natural rubber (STR5L)	Thai Hua Chumporn Natural Rubber Co., Ltd.
Tetraethoxysilane (A.R grade)	Sigma-Aldrich
<i>n</i> -hexylamine (A.R grade)	Sigma-Aldrich
<i>n</i> -butylamine (A.R grade)	Sigma-Aldrich
Tetrahydrofuran (A.R grade)	Fisher Scientific Ltd.
Chloroform (A.R grade)	BDH Chemicals Ltd.
Carbon tetrachloride (A.R grade)	BDH Chemicals Ltd.
Active zinc oxide (Commercial grade)	Pan Innovation Ltd.
Stearic acid (Commercial grade)	Imperial Industrial Chemicals Co. Ltd.
Polyethylene glycols (Commercial grade)	Pan Innovation Ltd.
Mercaptobenzothiazole disulfide (Commercial grade,)	Pan Innovation Ltd.
Bis-(3-triethoxysilylpropyl) tetrasulphide (Commercial grade)	Pan Innovation Ltd.
Silica (Hisil-255)	PPG-Siam Silica Co., Ltd.
Carbon black (N 550)	Thai Tokai Carbon Product Co., Ltd.
Calcium carbonate (CANANO P-62)	EMAX ASIA Co., Ltd.

3.2 Procedures

3.2.1 *In situ* Generation of the Silica in NR Matrix

NR sheets 10 g of 1-mm thickness were prepared by using a two-roll mill. Then, the rubber sheets were immersed in TEOS at room temperature for 3 h to obtain the swelling degree of 360% and the solvent (THF, CHCl₃, CCl₄) 100 ml was added. The NR solution was stirred at 600 rpm by mechanical stirrer for 24 h to obtain a homogeneous mixture at room temperature. The catalyst solution (*n*-butylamine and *n*-hexylamine) varied from 0.0640 M to 0.1860 M was added to conduct the sol-gel reaction of TEOS and the mole ratio of TEOS to water used for the range of 1:1.8 to 1: 3.0. The rubber solution was sampling every 24 h. Finally, rubber solution was precipitated in acetone. The *in situ* silica filled in NR was dried under vacuum at 40°C until the sample weight became constant.

3.2.2 Determination of *In situ* Silica Content in NR Matrix

Thermogravimetric analysis (TGA) was carried out using a TG/DTA PerkinElmer (Pyris Diamond) in order to determine the silica content in the *in situ* silica filled in NR. A sample of ca.10 mg was placed in a platinum pan and heated from room temperature up to 1000°C under air at a heating rate 10°C/min and air flow rate of 50 ml/min.

3.2.3 Preparation of Rubber Vulcanizates

The rubber compound was prepared by conventional mixing on a two-roll mill. To maintain the same silica particle size, the dilution method was used to prepare the uncured sample with various concentration of *in situ* silica. The master batch of *in situ* silica contents of 65 phr generated in NR sheet was produced from the use of 0.1395 M of *n*-hexylamine in THF and mole ratio of TEOS to water 1:2.7 under 50°C for 5 days was starting material and was diluted by the addition of virgin NR. The formulations of rubber compound are presented in Table 3.1. The cure time (t_{90}) was determined by Oscillation Die Rheometer. The vulcanization of the compounds was performed by a compression molding at 150°C under the pressure of 150 kg/m². The thickness of rubber vulcanizate was ca. 2 mm. In this study, NR vulcanizates with *in situ* silica, commercial silica, carbon black and calcium carbonate were represented by “In”, “Si”, “CB” and “Ca”, respectively and the filler content in a part by weight per hundred part of rubber (phr) was indicated by the number after the sample code.

Table 3.1 Formulations for rubber compounding in parts by weight per hundred parts of rubber (phr)

Ingredients	NR	In-15	In-30	In-45	In-65	In-30-C	Si-30	Si-30-C	CB-30	Ca-30
NR	100	100	100	100	100	100	100	100	100	100
<i>in situ</i> silica	-	15	30	45	65	30	-	-	-	-
Silica	-	-	-	-	-	-	30	30	-	-
Carbon black	-	-	-	-	-	-	-	-	30	-
CaCO ₃	-	-	-	-	-	-	-	-	-	30
Active zinc oxide	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2
MBTS ^a	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8	1.8
Sulfur	3	3	3	3	3	3	3	3	3	3
PEG ^b	-	0.5	1	1.5	2.2	1	1	1	-	-
Si-69 ^c	-	-	-	-	-	1.8	-	1.8	-	-

^a Mercaptobenzothiazole disulfide

^b Polyethylene glycol

^c bis-(3-triethoxysilylpropyl) tetrasulphide

3.2.4 Measurement of Mechanical Properties

3.2.4.1 Tensile Testing [41]

Tensile testing of rubber often involves application of a force to a sample and measurement of resultant deformation. In practice, stress-strain experiments are often carried out on a flat sample that has been shaped into form shown Figure 3.1.

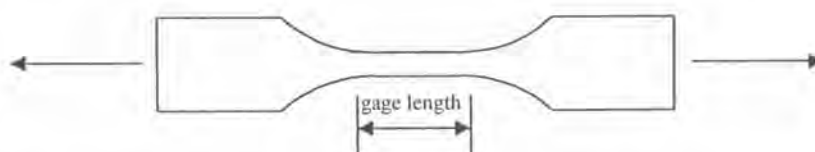


Figure 3.1 Typical shape of a flat polymer sample used for stress-strain test.

Two common modes of deformation (tensile and shear) shows in Figure 3.2. Stress is the force per unit cross sectional area (F/A). Strain is the deformation per unit of the original length ($\Delta L/L$) in tensile test or deformation per unit distance between the contacting surfaces (S/D) in shear tests. Stress is usually expressed in unit of newton per square meter (N/m^2). Strain is usually expressed in percent. Material stiffness is determined by modulus, which is defined as the ratio of stress to strain.

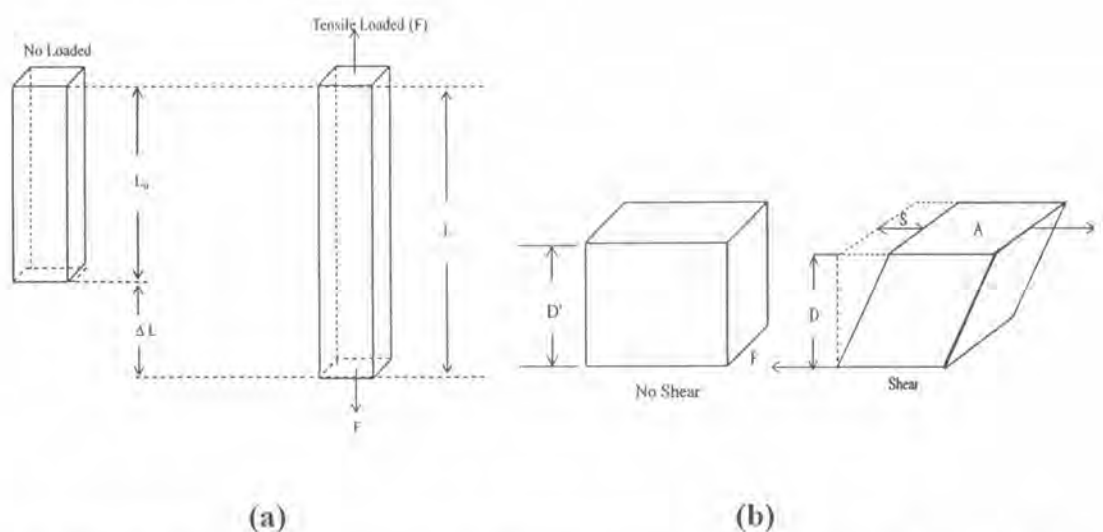


Figure 3.2 Modes of deformation a) Tensile stretching of a bar; b) Shear of a rectangular block.

In this study, the tensile properties were measured by a Lloyd Universal Testing Machine (model LR 10 K PLUS) according to ASTM D412 (A). The sample was stretched vertically in a symmetric fashion. The dumbbell sample used were 25 mm in gauge length, 25 mm in width and 2.0 mm in thickness. The crosshead speed was set at 500 mm/min with load cell 5 kN. The test was operated at room temperature. The values reported for each sample were based on an average of five measurements.

3.2.4.2 Hardness

Hardness, as applied to rubber, may be defined as the resistance to indentation under conditions which do not puncture the rubber. Hardness must be expressed in terms of instrument parameters rather than in basic units. The spring-loaded pocket durometer is the most common instrument for measuring hardness of elastomers. The shore durometer (ASTM D2240) in particular is generally used. In this instrument, the scale runs from zero hardness for a liquid to 100 for a hard plane surface such as glass. The type A durometer is used for soft stocks, up to a reading of 90. Above 90, the type D durometer having a different indenter shape and different stiffness spring is used.

In this study, the hardness testing was measured by using a Shore-type-A Lever Loader (REX GAUGE 2000 & OS-2 Stand) according to ASTM D 2240. The test temperature was carried out at room temperature. The measurements were taken from five different points distributed over the sample and the reported were based on an average of five measurements.

3.2.4.3 Abrasion Resistance [42]

Abrasion tests use an abradant to be applied to the surface of a rubber sample. Tested compounds are usually compared with a “volume loss” basis which is calculated from the weight loss and density of the compound. Abrasion test results are known to be variable; therefore, it is important to control and standardize the abradant used in the test. It is also required to relate the test results to a standard reference vulcanizate. The rubber test piece with a holder traverses a rotating cylinder covered with the specified abradant paper. By allowing the sample holder to move the test

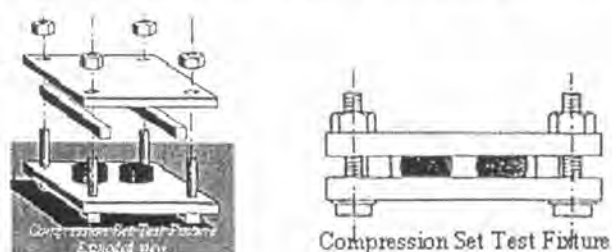
piece across the drum as it rotates, there is less chance of rubber build up on the abradant paper.

In this study, abrasion resistance was measured by Happen Abrasion according to DIN 53516 (ZWICK) at room temperature. The cylindrical in shape of samples used was 16 mm in diameter and had a minimum thickness of 6 mm.

3.2.4.4 Compression Set [43]

Compression set testing measures the ability of rubber to return to its original thickness after prolonged compressive stresses at a given temperature and deflection as illustrate in Figure 3.3. As a rubber material is compressed over time, it loses its ability to return to its original thickness. To determine the compression set, a cylindrical test sample is compressed by a percentage that is determined on the basis of its hardness and is then stored at a given temperature for a certain period of time in the compressed state. The temperature for the compression set test is a function of the material to be tested, its intended purpose and the test setup (e.g. 24 h at 70 °C for seals). 30 minutes after the pressure has been removed, the height of the sample is measured again and from this, the remaining deformation established. A compression set of 0 % means that the sample has attained its full original thickness again (something that is impossible in reality), while a compression set of 100 % means that the sample underwent complete deformation during the test and does not show any recovery.

The compression set in this study was measured according to ASTM D395. The thickness and diameter of the original sample was 6.0 mm and 13.0 mm, respectively. Sample was placed in an oven and compress to 25% strain at a 70°C for 22 h. Then, the sample was removed from the oven and allowed to cool for 30



minutes before measuring the final thickness.

Figure 3.3 The compression set testing device.

3.2.5 Dynamic Mechanical Analysis [44]

A dynamic mechanical analyser measures the stiffness and damping properties of a material. The stiffness depends on the mechanical properties of the material and its dimensions. It is frequently converted to a modulus to enable sample inter-comparisons. Damping is expressed in terms of $\tan \delta$ and is related to the amount of energy a material can store. DMA yields information about the mechanical properties of a sample placed in minor, usually sinusoidal and oscillating force as illustrate in Figure 3.4. DMA is the most sensitive technique for monitoring relaxation events, such as glass transitions, as the mechanical properties change dramatically when relaxation behavior is observed.

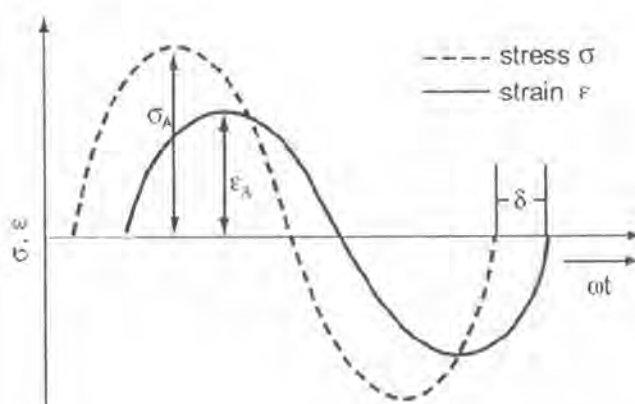


Figure 3.4 Sinusoidal oscillation and response of a linear-viscoelastic material; δ =phase angle.

Dynamic mechanical properties of rubber vulcanizates were measured under a tension mode at the frequency of 10 Hz by a dynamic mechanical analyzer GABO (EPLEXOR QC 25). Rectangular sample of 20 x 5 x 2 mm was subjected to sinusoidal loading heated from -100°C to 40°C at a heating rate of $10^{\circ}\text{C}/\text{min}$ and the dynamic strain was 0.5 %.

3.2.6 Determination of Network Chain Density [45]

The network chain density of the rubber vulcanizate was determined using a swelling method. The vulcanized rubber sample was cut to 20 x 20 x 2 mm sized pieces and weighed prior to swelling in toluene until it reached equilibrium (within 72 h.). Finally, the network chain density was calculated by using the Flory–Rehner equation as follows.

$$v_e = \frac{-[\ln(1-V_r) + V_r + \chi_1 V_r^2]}{\left[V_l \left(V_r^{\frac{1}{3}} - \frac{V_r}{2} \right) \right]} \quad (3.1)$$

where v_e is the network chain density (mol/ cm³), V_r is a volume fraction of rubber in a swollen sample calculated from Eq. (3.2), V_l is the molar volume of toluene (106.3 cm³/mol) and χ_1 is the Flory–Huggins interaction parameter between toluene and polymer (0.393).

$$V_r = \frac{\left[\frac{W_D - W_F}{\rho_s} \right]}{\left[\left(\frac{W_D + W_F}{\rho_D} \right) + \left(\frac{W_S}{\rho_s} \right) \right]} \quad (3.2)$$

where W_D and W_S are the weight of dry rubber and of solvent adsorbed by the sample, respectively, W_F is the weight of the filler in the sample, ρ_D is the density of the rubber vulcanizate and ρ_s is the density of toluene.

3.2.7 Morphology

3.2.7.1 Scanning Electron Microscopy (SEM)

In order to study the dispersion of silica particle in the NR matrix was observed through SEM investigations with a JEOL JSM 5410LM scanning electron microscope. The samples were sputter coated with gold in order to avoid the artifacts associated with sample charging. The acceleration voltage was 15 kV.

3.2.7.2 Transmission Electron Microscopy (TEM)

The dispersion and particle size of the filler in NR vulcanizates are studied by using TEM. Ultra thin films of the vulcanized rubber sample were prepared using a microtome (Boeckeler Instrument, Inc.) in liquid nitrogen. The rubber thin films were placed on a copper grid, which was coated by carbon. The transmission electron microscopy (TEM) observation was then carried out with a transmission electron JEOL JEM-2010 instrument of Hitachi Ltd. The accelerating voltage was 200 kV.